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14. ABSTRACT Support from the Army Research Office (ARO) has provided the opportunity for studies encompassing a combined effort consisting of different experimental and synthetic methods to produce novel nonlinear optical (NLO) materials with enhanced properties. This included the development of new synthetic branched organic macromolecules with different central core groups such as benzene, nitrogen, phosphorous, carbon as well as adamantane. These investigations gave the opportunity to probe the importance of the electronic coupling of the				
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## Report Title

### ABSTRACT

Support from the Army Research Office (ARO) has provided the opportunity for studies encompassing a combined effort consisting of different experimental and synthetic methods to produce novel nonlinear optical (NLO) materials with enhanced properties. This included the development of new synthetic branched organic macromolecules with different central core groups such as benzene, nitrogen, phosphorous, carbon as well as adamantane. These investigations gave the opportunity to probe the importance of the electronic coupling of the core unit to the NLO enhanced effect. The synthesis of novel metal nanoparticle topologies for the purpose of enhanced nonlinear transmission effects as well as nano-sensing applications was successful. This will included the synthesis of dendrimer metal nanocomposites where the PAMAM dendrimer may be considered as a host or a stabilizer. Fabrication of transition metal nanocomposite systems such as copper, gold, silver, as well as iron were carried out. The synthesis of chromophore functionalized dendrimer metal nanocomposites was carried out for the purpose of enhancing the optical nonlinear effects. Metal topologies such as silver and gold metal rods and spheres as well as metal clusters were investigated. New procedures to move these novel materials in to the solid state were carried out, which included the fabrication of stable films of the dendrimer metal nanocomposite materials.

Measurements with the novel materials were also carried out in conjunction with the design and fabrication of new branched, cyclic and two-dimensional structures and metal nanoparticle systems as to provide a direct feed back to the understanding of the structure/function relationships. The photo-physical measurements included investigations of the nonlinear transmission effect at a variety of wavelengths with use of an optical parametric oscillator system. This allowed the complete spectrum of the nonlinear effect to be evaluated in the visible to Infra-red spectral regions. The nonlinear transmission effects were coupled with measurements of degenerate-four-wave-mixing (DFWM) measurements at the same wide spectrum of wavelengths. This will gave valuable information regarding the real and imaginary parts of the nonlinear susceptibility. The measurement of the dynamics of the two-photon absorption as well as energy transfer processes were carried out with time-resolved transient absorption and time-resolved emission studies at both ultra-fast and nanosecond time-scales. The dynamics of the anisotropy decay and ultra-fast measurements of four-wave mixing (3-pulse photon echo) as well as investigations involving entangled two-photon absorption in the novel systems were carried out to probe the dephasing capabilities of the novel branched structures as well as in novel metal nano-topologies. The new materials and subsequent results provide valuable information regarding the optimization and discovery of NLO materials with enhanced properties.

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**List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

1. Goodson III, T. G. Optical Excitations in Organic Dendrimers Investigated by Time-Resolved and Nonlinear Optical Spectroscopy *Acc. Chem. Res.* 2005, 38, 99-107.
2. Goodson, T. Time-resolved spectroscopy of organic dendrimers and branched chromophores *Ann. Rev. Phys. Chem.* 2005, 56, 581-603.
3. Guda Ramakrishna; Dai, Q.; Zou, J.; Huo, Q.; Goodson, T. Interparticle Electromagnetic Coupling in Assembled Gold-Necklace Nanoparticles *J. Am. Chem. Soc.* 2007, 129, 1848-1849.
4. Guda, Ramakrishna; Goodson, T. Excited State Deactivation of Branched Two Photon Absorbing Chromophores: A Femtosecond Transient Absorption Investigation *J. Phys. Chem. A* 2007, 111, 993-1000.
5. Varnavski, O.; Yan, X.; Mongin, O.; Blanchard-Desce, M.; T. Goodson III Strongly interacting organic conjugated dendrimers with enhanced two-photon absorption *J. Phys. Chem. C* 2007, 111, 149-162.
6. A. Bhaskar, G. Ramakrishna, K. Hagedorn, O. Varnavski, E. Mena-Osteritz, P. Bäuerle, T. Goodson III "Enhancement of Two-Photon Absorption Cross Section in Macrocyclic Thiophenes with Cavities in the Nanometer Regime" *J. Phys. Chem. B* 2007, 111, 946-954.
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14. Yan, X.Z.; Goodson, T. High dielectric hyperbranched polyaniline materials *J. Phys. Chem. B* 2006, 110, 14667-14672.
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19. Varnavski, O.; Sukhomlinova, L.; Twieg, R.; Goodson III, T. Ultrafast Exciton Dynamics in a Branched Molecule Investigated by Time-Resolved Fluorescence, Transient Absorption, and Three-Pulse Photon Echo Peak Shift Measurements *J. Phys. Chem. B*, 2004, 108, 10484-10492.
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Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

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Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Ajit Bhaskar	0.25
Kevin Hagadorn	0.25
Jeff Raymond	0.15
<b>FTE Equivalent:</b>	<b>0.65</b>
<b>Total Number:</b>	<b>3</b>

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Dan Pederson	0.15
<b>FTE Equivalent:</b>	<b>0.15</b>
<b>Total Number:</b>	<b>1</b>

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Theodore Goodson	0.50	No
<b>FTE Equivalent:</b>	<b>0.50</b>	
<b>Total Number:</b>	<b>1</b>	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

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The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 1.00

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### Names of Personnel receiving masters degrees

NAME

Richard West

**Total Number:**

1

### Names of personnel receiving PhDs

NAME

Ajit Bhaskar

**Total Number:**

1

### Names of other research staff

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

**Total Number:**

### Sub Contractors (DD882)

### Inventions (DD882)

**Final Report**  
**Mechanistic Investigations of Branched Macromolecules and**  
**Metal Nanocomposites for Nonlinear Optical Applications**

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## **I. Summary of report**

Support from the Army Research Office (ARO) has provided the opportunity for studies encompassing a combined effort consisting of different experimental and synthetic methods to produce novel nonlinear optical (NLO) materials with enhanced properties. This included the development of new synthetic branched organic macromolecules with different central core groups such as benzene, nitrogen, phosphorous, carbon as well as adamantane. These investigations gave the opportunity to probe the importance of the electronic coupling of the core unit to the NLO enhanced effect. The synthesis of novel metal nanoparticle topologies for the purpose of enhanced nonlinear transmission effects as well as nano-sensing applications was successful. This will included the synthesis of dendrimer metal nanocomposites where the PAMAM dendrimer may be considered as a host or a stabilizer. Fabrication of transition metal nanocomposite systems such as copper, gold, silver, as well as iron were carried out. The synthesis of chromophore functionalized dendrimer metal nanocomposites was carried out for the purpose of enhancing the optical nonlinear effects. Metal topologies such as silver and gold metal rods and spheres as well as metal clusters were investigated. New procedures to move these novel materials in to the solid state were carried out, which included the fabrication of stable films of the dendrimer metal nanocomposite materials.

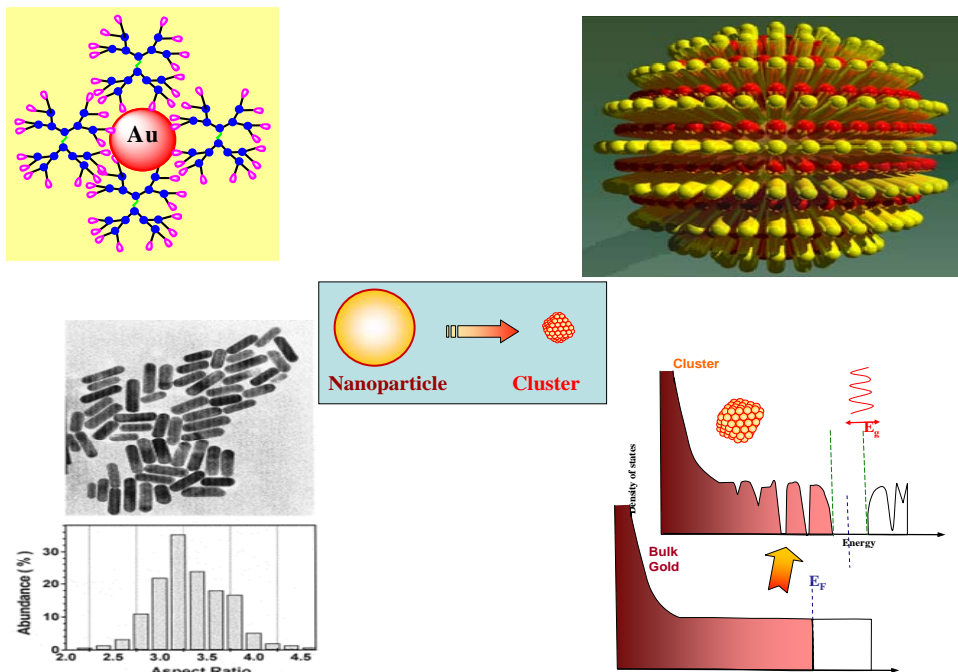
Measurements with the novel materials were also carried out in conjunction with the design and fabrication of new branched, cyclic and two-dimensional structures and metal nanoparticle systems as to provide a direct feed back to the understanding of the structure/function relationships. The

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## **II. Introduction**

The use of metal nanoparticles for applications in optical effects important to the mission of the Army has received great attention over the last decade. While the PI's laboratory has investigated metal particles with a size range of ~5 to 10 nm in the past in collaboration with the Army Research Office there is new enthusiasm for effects with smaller particles and clusters.<sup>1-10</sup> The reason for this new found interest stems from the observation that metallic nanoscale materials with a size close to the Fermi wavelength of an electron (less than 1 nm) tend to show quantum size effects<sup>-5</sup>. The research in this size regime is very attractive and is sparked by their appeal in technological applications as well as the fundamental thrust of scientific understanding of the behavior of nanoscopic materials<sup>11-13</sup>. Among several metal clusters, gold clusters are the extensively investigated systems. The PI's group has observed a transition from bulk-like

properties to molecular-like regimes leading to quantum confinement effects<sup>5-6</sup>. These gold clusters comprising tens of atoms to several hundred atoms have been synthesized by stabilizing



**Scheme 1:** *The focus of this grant was directed at new metal particle assemblies which give rise to enhance optical and electronic effects. This takes advantage of the PI's previous work in dendrimer metal nanocomposites, metal nanorods, chromophore encapsulated metal particles and small metal clusters of gold which show a band gap opening.*

them with alkyl or aryl thiolates and they are often referred as monolayer protected gold clusters (MPC). Quantization of energy as well as charge was observed for small size metal clusters and the electrochemical measurements have shown the size-dependent oxidation and reduction peaks<sup>14-15</sup>.

There is a real possibility to use these new gold clusters in a self assembly manner for new and interesting optical applications important to the mission of the Army. Although there has been extensive research on the electrochemical and electron-transfer properties with small sized MPCs, the research on optical, excited state dynamics and especially on the nonlinear optical properties are quite unexplored. Optical absorption and steady-state luminescence on the



MPCs has been investigated by Murray and co-workers<sup>16-18</sup>, as well as Tsukuda and co-workers<sup>19</sup> with several thiolate capped MPCs. The PI's laboratory has observed luminescence mainly in the near infrared region for several small sized MPCs. The nonlinear optical properties such as two-photon absorption (TPA) of these luminescent MPCs may give rise to potential applications in two-photon biological imaging, optical power limiting and nanolithography. And gives rise to new opportunities of forming aggregates and layered structures with these small metal clusters for enhanced effects.

One of the major limitations presently of using metal particles in optical and imaging applications stems from the fact that emission (luminescence) of gold particles is relatively small. Materials with the luminescence in near infrared region have found applications in biological imaging of breast-cancer tissue<sup>9</sup>. The PI's laboratory has discovered that these small size metal clusters such as Au<sub>25</sub><sup>\*</sup> have relatively good luminescence efficiency ( $\sim 2.5 \times 10^{-4}$ ) in the near infrared region, and can be made useful for two-photon imaging with infrared light. It should also be mentioned that the PI's laboratory has investigated the two-photon properties of the small metal clusters as well. And the use of scaling laws of TPA cross-section as the cluster size is decreased from a gold nanoparticle (4 nm) down to a Au<sub>25</sub> clusters (1.1 nm) may be utilized for the purpose of imaging and detectors.

The electronic structure and properties of these materials are also of great interest. Understanding of their detailed electronic states may allow one to tailor their properties for desired optical effects. The great complexity in the structural and electronic properties of these clusters becomes more apparent as their size decreases, leading to an intense interest and debate regarding the predictions of their properties. Also the lack of detailed experimental information regarding the broad cluster size dependence under the same cluster surface stabilizing conditions further hinders our understanding the science of nanometer-size metal clusters. There are some suggestions that nature of the stabilization molecules may play an important role in the electronic or surface (image) states of the small particles. For example, gold clusters can be stabilized to a remarkable degree by

a monolayer of ligands <sup>21</sup>offering an exciting possibility to fabricate building blocks for potential applications in catalysis <sup>22</sup>, biolabeling <sup>23</sup>, memory<sup>24</sup> and electronics based on single electron charging <sup>25,26</sup> with relative ease. With the monolayer protection of the thio type, it has been found that quantum size effects lead to a transition from bulk-like (metallic) behavior to a molecular-like behavior when the gold core size decreases below 3nm. This transition is particularly reflected in electrochemical and optical properties. The diameter range where this transition is expected to occur is quite broad: for gold nanoparticles with diameters less than 3 nm (~1000 atoms) the surface plasmon resonance (SPR) disappears and discrete peaks emerge in the UV-vis spectra for gold clusters with that are less than 1.1 nm (~50 atoms). Optical properties of nanoparticles with  $N > 1000$  can be described by a bulk dielectric function with appropriate corrections associated with electron scattering at the surface <sup>27,28</sup>. Smaller clusters with  $N < 40$  have shown a clear and discrete structure in their absorption and fluorescence excitation spectra. However, the transition in properties for sizes between ~50 and ~1000 atoms is not well understood. Careful analysis of absorption spectra for thiolate stabilized gold MPC indicated that HOMO-LUMO gap remains very large as compared to room temperature energy  $k_B T$  for sizes up to ~300 gold atoms. Moreover if the trend in the band gap dependence is close to what was predicted by the jellium model and experimentally demonstrated by Wyrwas <sup>29</sup>, we should expect the presence of substantial energy gap for clusters possessing much larger than 1000 atoms. Knowledge of the exact size where the band gap opening occurs is important as it has been previously shown that the catalytic efficiency of gold clusters supported on  $TiO_2$  has its maximum in this size region. Also in this region stable molecular-like MPC are expected to possess the highest electron self-exchange rates and conductivity in mixed-valent MPCs films. Finding larger stable clusters as well as layered or aggregate structures with a substantial electronic band gap have potentially important implications for the nanoelectronics based on MPCs. In order to understand many of the important details related to this materials the PI's laboratory has systematically investigated the femtosecond optical excitation

dynamics in gold clusters capped with hexane thiolate as a function of the particle size in the range 1.1 nm – 4 nm (~25-2500 gold atoms) to unravel the critical size where the opening of band gap occurs. We have used the power of two-photon optical spectroscopy, ultrafast time-resolved fluorescence and transient absorption to shed more light on the size dependent dynamics of gold clusters and consequent transitions in optical properties. This has helped in predicting the properties of not only the isolated metal clusters but also the properties of the self-assembly metal cluster systems (see below).

The self-assembly properties of metal particles has been investigated in a number of different materials and topologies. The use of gold and silver metal aggregates has been extensively by various synthetic methods. There has been a great deal of interest recently in the self-assembly properties of gold and silver particles for enhanced emission and Raman effects. For example, the plasmonic properties of triangular nanoprisms have been investigated using dark-field optical microscopy. These effects are only observed in the prepared aggregates only with particular geometries. There has been also templating methods for preparing metal aggregates with particular geometries with relatively interesting and highly productive organic materials.<sup>30</sup> For example, the use of organic dendrimers as templates for making metal particle aggregates proved to be very useful in preparing very productive optical limiting materials for the visible and infra-red spectral regions. The ability of PAMAM dendrimers to cooperate the metal particles in to particular aggregates of defined size is a great accomplishment and opens up new ideas toward the creation of defined metal aggregates with properties that may scale as size of aggregate. New methods to prepare aggregates and layered structures are expected to yield new and interesting enhanced properties in these small cluster systems. Indeed, the investigation of the small metal clusters along with the self assembled properties offers new avenues toward creating materials for particular optical and electronic devices. However, the understanding of the important parameters in these materials is still very limited. Thus, investigations of the isolated and self

assembled (aggregate) behavior are needed in order to prepare new and productive materials for future Army applications.

### **III. Results from Support by Army Research Office**

Presently, the motivation for the creation of nanomaterials and real applications for department of defense have merged to a point of particular interest for specific directions. One of these areas involves improving the materials aspects of optical limiting devices. The development of metal particles systems as well as conjugated organic molecules with large two-photon absorption (2PA) cross-sections<sup>31,32</sup> is of broad interest to many areas of research and development and is related to the current defense interest in optical limiting. Other applications which may also take advantage of materials with superior 2PA properties are 3D microfabrication<sup>33-36</sup>, photodynamic therapy<sup>37</sup>, two-photon microscopy<sup>38-41</sup>, and optical data storage<sup>42-44</sup>. In order to realize these applications, novel molecules with large 2PA cross sections in the visible, near infrared and telecommunication wavelengths are desired. And it has been our approach during support from the Army Research Office over the last years to utilize metallic particle and branched structures for this purpose.<sup>45-79</sup> These materials have shown an enhanced two-photon cross-section.<sup>45,46,48-50, 54-56,61-63,65</sup>

While the present proposal is not directed toward organic optical materials it is important to summarize here the investigations we have carried out in the past on organic materials supported by the Army Research Office. Because of some of these investigations, there are now several design approaches for the synthesis of organic molecules with large 2PA cross-sections. In the past molecules with dipolar and quadrupolar character have been the focus of development.<sup>80-92</sup> Numerous dipolar chromophores have been synthesized with varying donor-acceptor configurations, as well as different  $\pi$ -bridging centers, and different donor-acceptor strengths so as to probe the structure and 2PA property relationships.<sup>31-40</sup> Recent investigations indicate that increasing the dimensionality of donor-acceptor molecules is a good approach as certain branched systems exhibit enhanced 2PA cross-sections over the linear

counterparts.<sup>93-94</sup> This is believed to be a consequence of cooperative interaction among the individual arms<sup>94</sup>. The interest in multiple branched systems for 2PA also stems from the fact that relatively large 2PA cross-sections may primarily be realized from low lying excited states. Consequently, considerable research has been carried out towards the design and synthesis of multiple branched chromophores. Several configurations such as donor- $\pi$ -acceptor, acceptor- $\pi$ -donor, chromophores with different branching centers,  $\pi$ -bridging units, tri and tetra branched structures have been synthesized and studied.<sup>95-106</sup>

From the PI's work supported by ARO it is now clear that although larger donor-acceptor strength is important for higher 2PA cross-section, the nature and length of the linker does play a decisive role in increasing the 2PA cross-section and nonlinear optical (NLO) properties. It has been shown in dipolar chromophores that richer  $\pi$ -electron systems improve the intramolecular charge transfer character and thereby enhances the NLO properties<sup>107</sup>. Several  $\pi$ -bridging chromophores have been considered for improving the 2PA cross-section. Among them, alkene  $\pi$ -bridging is most widely studied and it has been suggested that in many of the linear systems, alkene- $\pi$ -bridging is better over alkyne  $\pi$ -bridging.<sup>108,109</sup> However, due to several reasons pertaining to intra-arm electronic coupling, charge delocalization and charge transfer, the consequences of  $\pi$ -bridging on NLO and 2PA properties in branched systems may be different from the linear quadrupolar molecules.<sup>110-113</sup> It has been theoretically predicted from *ab-initio* calculations that the 2PA cross-sections of alkyne  $\pi$ -bridging containing quadrupolar molecules are not significantly different from their alkene  $\pi$ -bridging analogues.<sup>112,113</sup> However, more investigating in different aggregates with different  $\pi$ -bridging is necessary to fully utilize the "building-block" approach for superior optical limiting applications.

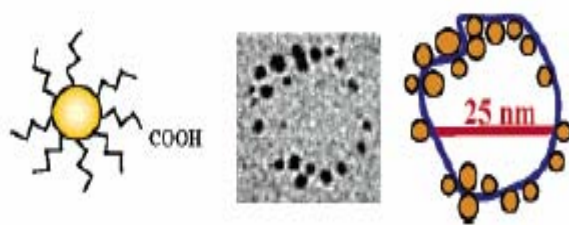
Time-resolved (fluorescence, transient absorption, and 3-pulse photon echo) have also been very important in explaining the connection between the delocalization length and the enhancement in the 2PA cross-section. It has been found from these investigations (supported by ARO in the PI's lab) that we should go beyond the weak interaction limit to highly delocalized excitations

where many chromophores within the system are coherently coupled in order to create superior 2PA and optical limiting systems. The problem of excitation delocalization length was intensively studied previously for linear polymers,<sup>114-119</sup> natural photosynthetic antennas,<sup>120-122</sup> J-aggregates.<sup>123-125</sup> Dendrimers (and other branched structures) are more ordered systems than linear polymers and due to specific structure they can accommodate more chromophores in a small volume. This makes strongly interacting dendrimers with large number of coherently coupled conjugated linear blocks very prospective for nonlinear optical applications. There is no single experimental method to detect the coherent domain size. This problem intrinsically requires a multi technique approach. The number of coherently coupled repeat units is now more or less established in most important linear polymer systems although many details remain to be clarified. This parameter is unknown for most of the large (larger than trimer) branched conjugated systems. We reliably prove the presence of the excitations delocalized over 9 branches in a large new dendrimer at room temperature. We also illustrated the very different spectroscopic properties (static and dynamic) of this dendrimer system as compared to those of widely investigated phenylacetylene dendrimer.<sup>126-128</sup> Specific structure of electronic interactions associated with meta-substitution on a phenyl ring results in fairly different “**spectroscopic units**” in the ground and excited states configurations with excitations localized on a single tolane segment in the ground state geometry<sup>126-128</sup>(which is relevant for instantaneous TPA).

#### **A. Investigations with New Metal Particle Topologies**

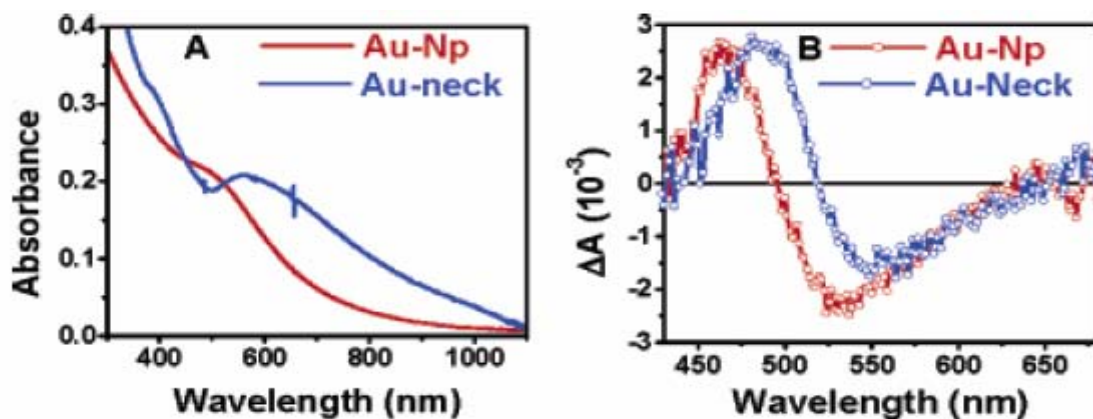
The PI's laboratory has always been interested in the use of different metal aggregates for novel optical effects important to the Army Research Office. In particular, we have investigated the possibility of enhancement of optical nonlinear effects due to the coupling of metal particle two-photon absorption in a particular geometry. In our previously supported studies supported by ARO, we examined the nature of the electromagnetic coupling and its influence on nonlinear properties of these Au-necklace particles (Au-neck) with the aid of time-resolved spectroscopy.<sup>5,6</sup> Comparisons were made with monocarboxylated

Au nanoparticles (Au-Np) (structures are shown in figure 1). The syntheses of the Au-neck and monocarboxylated gold-NP were provided by Professor Ho of Central Florida University. From the TEM measurements it can be observed that these particles consist of nanoparticles of 2-3 nm size and are connected very close to each other in the form of a necklace. Figure 2 shows the optical absorption spectra of Au-Np and Au-neck dispersed in dichloromethane/methanol (2/1 v/v) and 1% trifluoroacetic acid. It can be observed that the Au-Nps show a surface plasmon resonance peak, which is common to Au



**Figure 1:** The metal particle (gold) sphere and chain topologies.

nanoparticles of this size. Interestingly, the Au-neck particles show a slightly red shifted and broader plasmon absorption with respect to spherical Au nanoparticles, suggesting electronic interaction with close lying Au nanoparticles. A similar absorption spectrum has been observed for Au-DNA nanocomposites and has also been ascribed to static electromagnetic coupling between neighboring Au nanoparticles.<sup>129</sup> Two color pump-probe measurements<sup>14</sup> have been carried out on these organized Au-neck particles, and the corresponding electron dynamics has been compared with the dynamics found in Au-Np. Shown in Figure 2 are the transient absorption spectra of both Au-Np and Au-neck at a time delay of 500 fs after excitation at 390 nm. Similar to what has been observed for Au nanoparticles, 15 Au-Nps have shown a negative



**Figure 2:** *The metal particle topology absorption and the transient absorption spectra.*

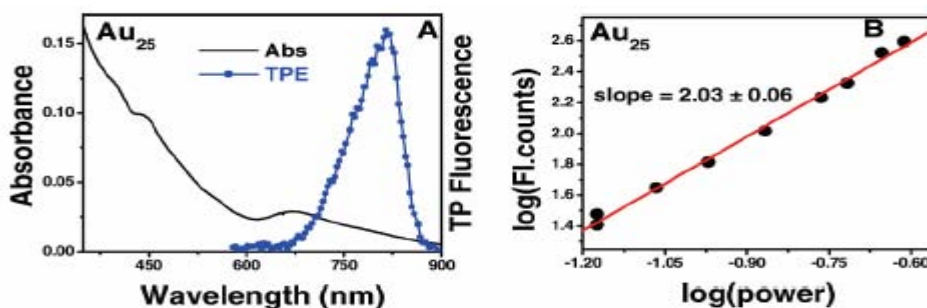
absorption in the region of 480-600 nm with a maximum at 530 nm and a positive absorption with a maximum at 470 nm. Analogous transient absorption features are observed for the Au-neck, except both the bleach maximum and absorption maximum are shifted to longer wavelengths (550 and 500 nm, respectively). This shift to longer wavelengths is consistent with the optical absorption maximum and most likely arises from the electromagnetic interaction from the static electronic coupling between the neighboring particles in the Au-neck. It has been observed that, as the time delay is increased from 100 to 800 fs for the case of Au-neck, both positive absorption and bleach have increased in amplitude, while a decay of surface plasmon bleach is observed in case of Au-Np. The growth of surface plasmon bleach has been observed in previous ultrafast measurements of Au nanoparticles and is explained by electron-electron scattering, which occurs on a time scale of 100-500 fs. After the electron-electron scattering, the hot electrons relax with a decay profile which has two components related to electron-phonon and phonon-phonon relaxation processes. The kinetics shows the electron-electron scattering, which is considerably slower for the Au-neck than the Au-Np. This could arise from efficient dipolar coupling between the plasmons of two neighboring particles. In addition to this, the recovery of bleach is also found to be substantially slower for the Au-neck over the Au-Np. Pump-power dependent measurements on Au-neck and Au-Np have shown that the



electron-electron scattering is weakly dependent on pump-power for Au-neck while electron-phonon relaxation dynamics is very much dependent on pump-power. The critical conclusion here is that the metal particle assembly shows that inter-particle interactions can give rise to changes in the dynamics and other optical properties when designed with the appropriate criteria.

### **b. Transition in properties as particles change in size to small metal clusters**

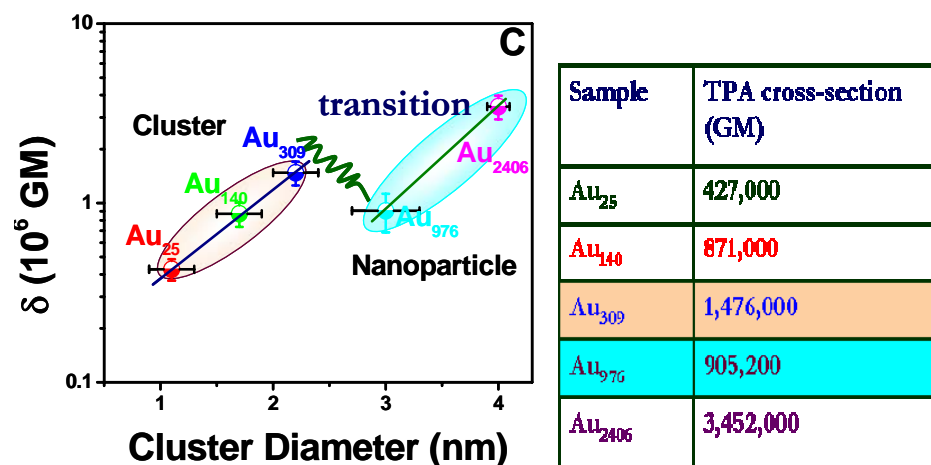
It is clear that materials with the luminescence in near-infrared region have found applications in biological imaging of breast-cancer tissue.<sup>9</sup> Since small-size metal clusters such as Au<sub>25</sub>\* have decent luminescence efficiencies ( $2.5 \times 10^{-4}$ ) in the near-infrared region, they can be made useful for two-photon imaging with infrared light. In this context, we have investigated the two-photon emission and cross-section of Au<sub>25</sub> clusters with infrared light. In addition, the present investigation is aimed at understanding the scaling laws of TPA cross-section as the cluster size is decreased from a gold nanoparticle (4 nm) down to Au<sub>25</sub> clusters (1.1 nm). Shown in Figure 3 are the optical absorption and steady-state emission spectra obtained for Au<sub>25</sub> clusters capped with hexane thiolate and dissolved in hexane. Absorption spanning the visible to near infrared region is seen for Au<sub>25</sub> with distinct maxima around 675 and 410 nm and the ultraviolet region. The observed absorption spectra matched well with the previous reports and are ascribed to the quantized nature of the gold clusters. Also shown in



**Figure 3:** The metal cluster absorption and two-photon absorption spectra<sup>7</sup>

Figure 3 is the emission spectrum obtained after excitation at 1290 nm from the output of an optical parametric amplifier which shows the emission with a

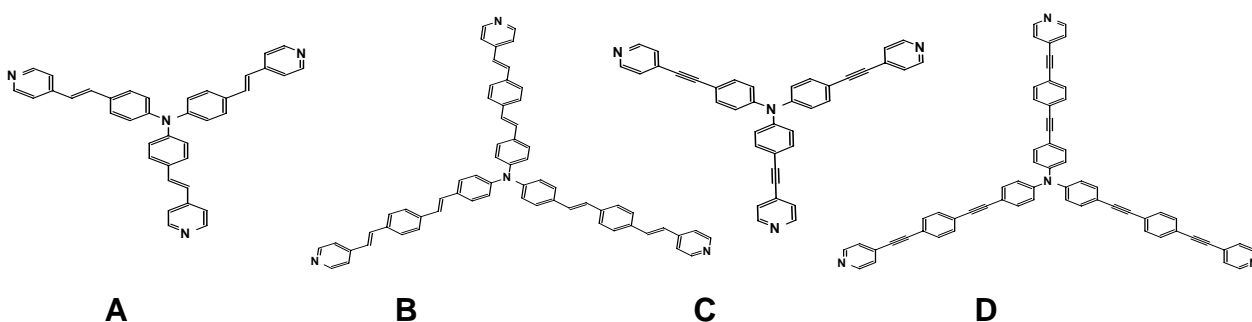
maximum at 830 nm. The corresponding pump-power dependence of the fluorescence at 830 nm is shown in Figure 4 which gave a slope of 2 indicating that it is a two-photon excited emission. Comparative TPA cross-section measurements have been carried out using the two-photon excited fluorescence method<sup>10</sup> with H<sub>2</sub>TPP in toluene<sup>1</sup> as the standard. From these measurements, TPA cross-section at 1290 nm for Au<sub>25</sub> in hexane was determined to be 2700 GM which is superior to the TPA cross-sections of many organic chromophores with emission in the near-infrared region. These initial measurements on Au<sub>25</sub> gold clusters suggest that they can be used as multiphoton imaging agents with near-infrared luminescence. Measurements with a number of different size particles showed an interesting trend which includes a gap in the trend in the vicinity of ~1.5 to 2 nm. Shown in figure 4 are the two-photon cross-section results for the different size particles



**Figure 4:** The results of different size metal particles. A gap in the trend is observed at ~2 nm.

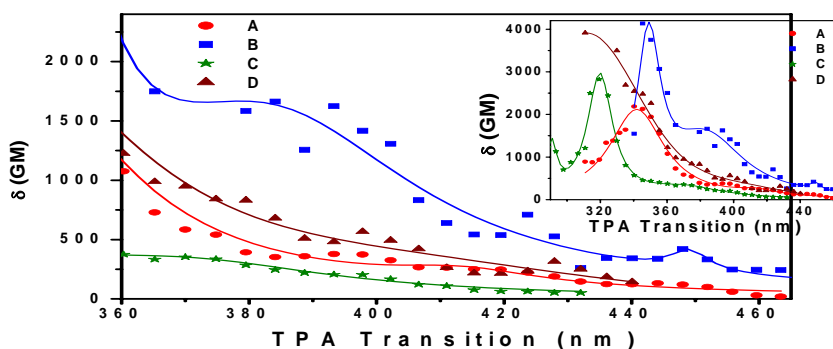
obtained from two-photon fluorescence measurements with fs pulses. The gap in the trend is obvious and suggests a change in properties on going to smaller cluster sizes. We have also carried out time-resolved measurements with these interesting new small metal clusters as well. Both time-resolved transient absorption and time-resolved fluorescence upconversion have shown the important transition from bulk metal behavior to quantized small (molecular orbital) behavior in the same vicinity of cluster size.

**c. Novel Branched Structures for large TPA applications.**



**Figure 5.** Branched chromophores studied for optical limiting effects

We have carried out two-photon absorption cross-section measurements on the branched structures shown in figure 6 using two-photon excited fluorescence (TPEF) as well as with our non-degenerate 2PA setup.<sup>56</sup> Figure 7 shows the 2PA cross-section spectrum for chromophores **A** through **D**, the cross-sections are plotted versus the transition energy expressed in wavelength. As a comparison, the cross-sections at 770 or 800 nm (at the maximum of lowest energy absorption band) for the molecules are listed in Table 1 as well (shown in parentheses are the non-degenerate 2PA cross-sections at those wavelengths). It is worth reiterating that non-degenerate 2PA has shown larger than 2PA at equivalent values for degenerate excitation. For this reason the values in Table 1 have been reduced by an appropriate scaling factor to make a more direct comparison with the degenerate 2PA cross-sections<sup>130</sup>.



**Figure 6:** The non-degenerate 2PA spectra of the molecules in figure 5.

There are several comparisons that can be made regarding the 2PA properties observed in these systems. First, a comparison between the linear and nonlinear absorption spectra reveals that all the molecules exhibit substantial

2PA into the lowest energy absorption band (i.e. 380 – 450 nm) which is both one and two-photon allowed. There also exists a stronger, higher energy two-photon allowed state which lies in between the two one-photon bands, which has been attributed to strong electronic coupling between the branches. Furthermore, the trends observed for both the degenerate and non-degenerate cross-sections in Table 1 are quite similar. The two alkene containing systems (**A** and **B**) differ only by an increase in the conjugation length of the individual arm by one vinylene unit. In the lowest energy absorption band, one observes a three-fold increase in 2PA cross section for **B** in comparison to **A**. The same trends can be noted for compounds **C** and **D** which both contain alkynes. Increase in conjugation reduces the detuning term (the energy difference between the ground and first excited state and the ground and TPA state) in the sum-over-states expression and also increases the transition dipole moment. As a result of these two contributions, the 2PA cross section increases significantly. Comparing chromophores **B** and **D**, which contain similar chromophore density, it is clearly seen that the 2PA of the alkene branched system **B** is approximately 3.7 times higher than its alkyne counterpart **D**. Similarly, the ratio of 2PA cross-section between **A** and **C** is 4. A direct comparison between molecular systems can be made by normalizing the cross-sections listed in Table 1 to their respective molecular weights. Still, the alkene chromophores show a 4-fold increase in 2PA cross section when compared to the corresponding alkynes at the low energy peak.

A surprising trend was observed when considering the high energy two photon absorption band shown in the inset of Figure 6. When we compare **A** and **B**, there is an increase in the 2PA cross-section by a factor of 2 and about 1.5 when **C** and **D** are compared suggesting the effect of conjugation length. As the conjugation length is increased, the absorption transition dipole moment is increased (Table 1) and the detuning factor is decreased there by influencing the 2PA cross-section. It is interesting to see the trend observed in 2PA cross-section to high energy states for alkene and alkyne -bridging branched chromophores. When we compare **A** and **C**, the alkyne -bridged chromophore's

(C) cross-section is around 1.4 times higher than corresponding alkene analogue (A). As mentioned above, the expected trend in transition moments suggest that the TPA in the alkene systems to be longer. This is contrary to what the steady-state results predicted. However, ultrafast time-resolved measurements, which give the information of excited state characteristics, are able to probe these differences. It is to be noted here that when 2PA cross-section to higher energy states are concerned, it involves the knowledge of excited state transition dipole moment (from sum over states formalism). Estimates of excited state transition dipole moment can be obtained from ultrafast transient absorption measurements as was done in these investigations.

**Table 1:** Summary of linear and nonlinear optical properties of the chromophores.

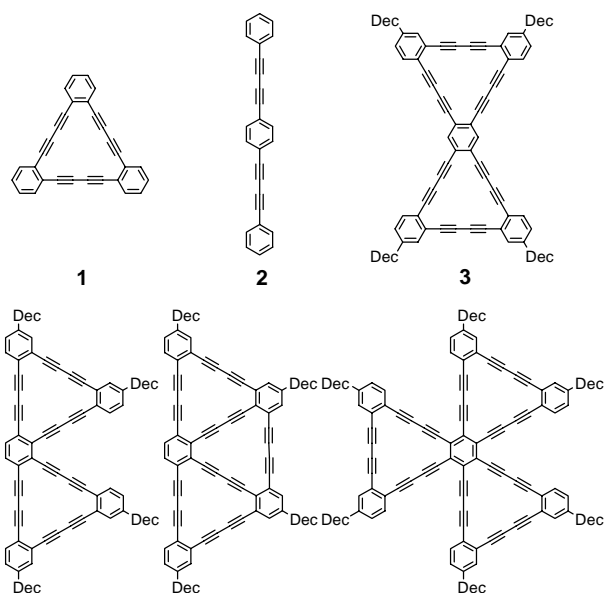
Molecule	$\lambda_{\text{abs}}(\text{nm})$	$\lambda_{\text{em}}(\text{nm})$	$\delta$ (GM)	$\eta$	$\tau_r$ (ns)	$\mu$ (D)
A	406	479	<sup>a</sup> 370 (187)	0.23	10	3.3
B	426	519	<sup>a</sup> 1037 (812)	0.26	8	3.9
C	377	428	<sup>b</sup> 91 (102)	0.58	2.7	5.6
D	391	455	<sup>a</sup> 280 (283)	0.55	2.7	5.8
N(DSB) <sub>3</sub>	419	484	<sup>a</sup> 270	0.48	3	5.9
PRL-701	422	502	<sup>a</sup> 491	0.51	2.9	5.5

<sup>a</sup>800 nm excitation, <sup>b</sup>770 nm excitation. Values in parentheses are from non-degenerate pump probe measurements;  $\lambda_{\text{abs}}$ ,  $\lambda_{\text{em}}$  are absorption and emission maxima respectively;  $\delta$  is 2PA cross-section,  $\eta$  is the fluorescence quantum yield;  $\tau_r$  is the radiative lifetime and  $\mu$  is the emission transition dipole moment calculated from Strickler-Berg formula.

#### d. Building Symmetric Two-Dimensional Two-Photon Materials

We have also investigated large, flat, graphyne-like networks with promising and exciting electronic and optical properties.<sup>54,59</sup> They are also attractive from a nonlinear optical standpoint. However, due to synthetic and processing challenges, the complete network has never been synthesized,

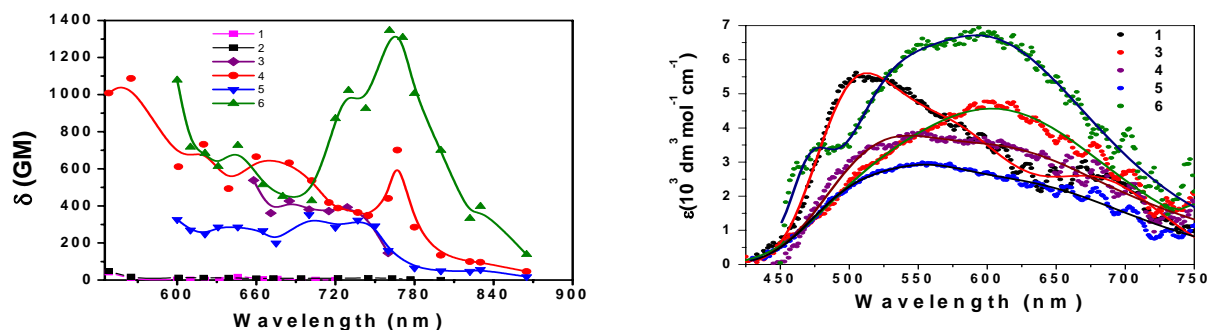
instead we have applied a building block approach to understand the nonlinear optical properties of such graphyne systems. Using bis-annulene building blocks, we have investigated a number of chromophores shown in figure 7.<sup>54</sup> The way in which building blocks are assembled to yield novel architectures with enhanced TPA cross sections significantly also impacts the excited state characteristics and subsequently, the TPA cross sections of the resulting macrostructures. The TPA properties of six bisannulene carbon networks (BCNs) have been measured. Their one-photon



**Figure 7.** Structures of two-dimensional bis-annulenes studied.

photophysics were also investigated using UV-Vis, fluorescence and transient absorption measurements. Significant differences were observed in the steady state properties of the molecules, leading to intriguing trends in the TPA behavior. We have correlated their linear and nonlinear optical behavior based on experimental results by proposing a model that correlates the molecular symmetry of the molecules to the nature and energetic locations of excited states. The observations are in accordance with previously published theoretical treatment of the molecules.<sup>59</sup> Here,  $\delta_{\max}$  is the maximum TPA cross-section,  $\delta'$  represents the TPA cross-section per unit  $\pi$ -electron,  $E_{ge}$ ,  $E_{ge'}$  are the energy differences corresponding to one-photon and two-photon maxima. We found a very large cross-section for the radiation symbol molecule. The value is very

large and considering that there are no electron donating or acceptor groups are attached to the molecules, they may be among the largest reported.



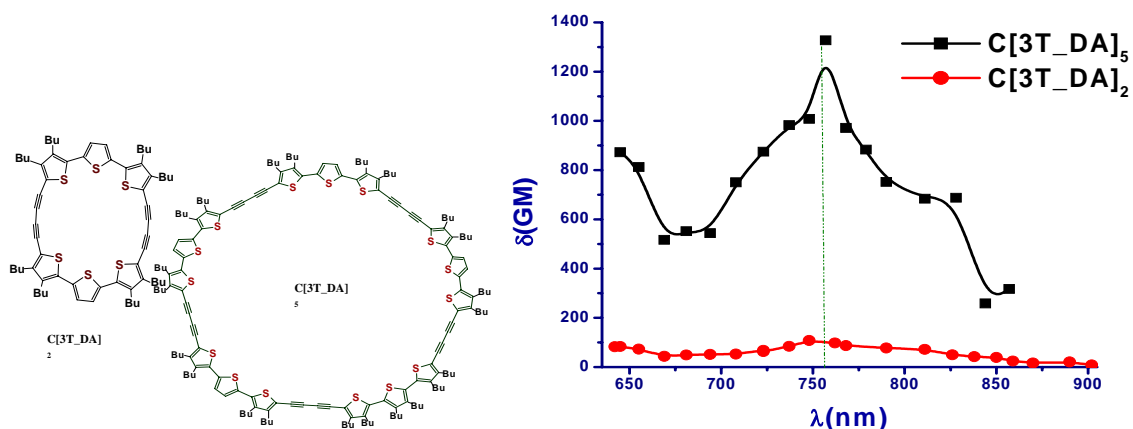
**Figure 8.** A) TPA cross section spectra and B) Excited state absorption spectra obtained from femtosecond transient absorption measurements for all the annulenes studied.

In order to understand the mechanism of the large 2PA cross-sections in these systems we carried out time-resolved transient absorption measurements shown in figure 8. These measurements allowed us to extract the transition moments in these systems as a function of the overall symmetry of the system. Indeed, the radiation symbol showed a high degree of symmetry in the ground state, and upon excitation the breaking of symmetry allows for a number of different possible states which can be populated by the two-photon excitation.<sup>54</sup> It is with this understanding that we believe this new topology of molecular aggregates may be the a VERY promising direction for creating all organic new optical limiting materials with high scalability!

#### e. Enhancement of Two-Photon Absorption Cross Section in Cyclic Thiophene Cavities with Tunable Size

We have investigated thiophenes in a new, circular geometry (Figure 9).<sup>70</sup> The circular geometry presents us with the possibility of complete conjugation. Linear macromolecules have defects which hinder conjugation over the entire chain. This seems less likely in case of circular chromophores since there are no “end-effects”. We have studied the nonlinear optical properties of two

macrocyclic thiophenes. Their TPA cross section ( $\delta$ ) spectra were measured using Two-photon excited fluorescence (TPEF) method. We have also investigated the fluorescence dynamics and the excited state dynamics in these chromophores. These systems are equally interesting from a theoretical standpoint. It has been proposed from previous theoretical computations that these cyclic thiophenes have two different electronic energy levels.<sup>131-133</sup> According to the energy diagram as the ring size increases, the coupling between the higher excited states and the first excited state ( $S_1$ ) becomes more efficient.<sup>131</sup> TPA results showed a 550% enhancement in the TPA cross section of a single C[3T\_DA]<sub>2</sub> unit upon increasing the ring size. Femtosecond fluorescence upconversion measurements have shown the presence of coherent energy transfer in both macrocycles, resulting in complete delocalization of the excitation over the entire ring in both macrocycles.<sup>70</sup>



**Figure 9.** Structures of the cyclic thiophenes and the 2PA results of the systems studied in this investigation.

These investigations in all have been very useful in discovering new materials and even new applications for the two-photon and optical limiting effects important to the ARO. They have helped train more than 5 graduate students and 4 postdoctoral fellows in part. We have published a large number of paper with this previous support and give many lectures and conference presentations with the results obtained from our investigations. We are very grateful for the support of ARO in our previous work.



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